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[54] The name of the invention: A catalyst of activated carbon containing iodine and the method to remove and reclaim sulfur dioxide in the industrial exhaust gas with the said catalyst

[57]: Abstract

A catalyst of activated carbon containing iodine and the method used to eliminate and reclaim sulfur dioxide in the industrial exhaust gas with said catalyst comprising these following main stages: dust removal, adsorptions and oxidation, water-washing regeneration and concentrating and so on. This method can effectively eliminate the pollution caused by the exhaust gas from the Sulfur Acid Factory, Smelting Factory, Chemical industry and PowerStation, and moreover, can recycle sulfur acid with 20-30% concentration. This method is particularly suitable for dealing with the exhaust gas containing a great deal of dust and the low concentration sulfur dioxide.

What is claimed

1. A catalyst of activated carbon containing iodine employed to desulfurization, characterized in that the total pore volume of said activated carbon is 0.60-0.75cc/g, surface area of said activated carbon is 550-750m^2/g, the active component iodine may be iodine or potassium iodide, sodium iodide, ammonium iodine, potassium iodine and other iodide, in which iodine content is 0.15-0.60wt%;
2. A method employed to extract sulfur dioxide from exhaust gas by catalyst of activated carbon containing iodine, characterized in:
   1) If the active component is iodine, said iodine can be attached to the activated carbon by the method sublimation and fumigation.
   2) If the active component is iodine containing compound, said iodine can be attached to the activated carbon by soaking the activated carbon into its aqueous or ethanol solution and then drying it in the 100-160 hot air after soak.
3. A method to extract sulfur dioxide from exhaust gas by said catalyst according to claim 1or 2 comprising the following main three stages which are: 1 dust removal from the exhaust gas, 2. adsorption and oxidation and regeneration, 3 concentrating sulfuric acid reclaimed, wherein said the adsorption and oxidation is done in the multiple towers, and the temperature of exhaust gas is kept within 50-70 when the exhaust gas is adsorbed and oxidized in the adsorption tower.
4. The method according to claim 3, wherein the process of regeneration is: right after being washed by dilute sulfuric acid of different concentration and water, the grade bed of catalyst is soaked into water for a certain time.
5. The process of regeneration according to claim 3, wherein, air is firstly pumped into the catalyst to oxidize the iodine ion contained in the grade bed of catalyst into iodine, before regeneration.
6. The process of water washing regeneration about catalyst according to claim 3 or 4, wherein, the water vapor that has been heated to 90 - 100 is pumped into the catalyst tower to complete the process of regeneration, after water washing regeneration .
7. The process of water washing regeneration according to claim 3, wherein when the activity of catalyst is decreased, the active component should be compensated after said process of water washing regeneration, said compensation is carried out by adding the measured iodide solution from the top of catalyst tower.

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The present invention relates to a catalyst of activated carbon containing iodine and the method to turn the sulfur dioxide from coal-fired flue gas into sulfuric acid and thus reclaim it. This method is particularly suitable for eliminating sulfur from the exhaust gas containing low concentration sulfur dioxide and for the purification process.

In industrial field, the exhaust gas from the Sulfur Acid Factory, Smelting Factory, Chemical industry and PowerStation usually contains a certain amount of sulfur dioxide. These exhaust gas from the industrial field causes serious pollution to the environment. To eliminate this influence, the process of catalyzing and oxidizing is often adopted to oxidize sulfur dioxide in the exhaust gas into Sulfur Acid and reclaim it, thus the pollution caused by sulfur dioxide will be eliminated. , The closely related method in the present invention is the process of using the activated carbon containing iodine as catalyst, for example, the method of the activated carbon containing iodine as proposed in the West Germany patent (GB1139817) to recycle the sulfur dioxide from the exhaust gas. However this method of preparing catalyst and the reaction operating are very complicated, and the method of continuously recycling high concentration Sulfur Acid to inhibit the loss of iodine ion, which makes it very difficult to adopt this process in the common factory. In the UK patent BP1090306, in order to decrease the loss of iodine, the process of the adsorption and regeneration is separated, and ammonia water and pure water have to be successively used to wash regeneration so as to maintain the activity of catalyst. The American DU PONT Company proposed the method of using activated carbon containing iodine as the catalyst to treat exhaust gas from Sulfur Acid Factory (Scholte ,W,AICHE 67th Annual meeting Vol 13 85B, 1974). This method needs to recycle the hydrogen iodide from the washing solution of regeneration, so as to be continuously supplemented into the grade bed of catalyst to keep the iodine content in activated carbon around 6%, thus to maintain activity of catalyst. In this method the loss of iodine is serious, and the operation of circularly supplementing iodine is complicated. In these known technologies, the iodine content in activated carbon is relatively high, and the loss of iodine is pretty high during operation. So far, there are still no simple and practical measures in known methods. Furthermore, the stability of catalyst is less satisfying, and it is very difficult to employ this method to purify the exhaust gas containing high concentration dust, for example, the exhaust gas containing high concentration dust from the Smelting Factory or PowerStation which use coal as fuel, due to serious catalyst poisoning.

One object of the present invention is to prepare a kind of catalyst of activated carbon containing low concentration iodine and with high stability and to figure out a method to eliminate and recycle sulfur dioxide from exhaust gas. The method and catalyst in this invention can be applied to recycle sulfur dioxide not only from the dust-free gas exhausted from sulphuric acid plants and other chemical industries, but also from the exhaust gas of coal-fired which still contains slightly less than $0.2g/m^3$ dust even after dust removal and other industrial exhaust gas containing sulfur dioxide.

In present invention, the content of iodine in the catalyst is 0.15-0.6wt%. The physical properties of activated carbon are as follows: intensity is more than 90%, pore volume is 0.60-0.75 cc/g, surface area is 550-750 m^2/g, bulk density 508-520 g/l. The active component attached to the activated carbon may be iodine or iodide, such as potassium iodide, sodium iodide and ammonium iodine.

The method to prepare catalyst is as follows:

1 If the active component is iodine, said iodine can be attached on the activated carbon by the sublimation of iodine.

2, If the active component is iodine containing compound, said iodine can be attached to the activated carbon by soaking the activated carbon into its aqueous solution or ethanol solution□and then drying it in the 100-160□hot air after soak.

The process to eliminate sulfur dioxide with the catalyst of activated carbon comprises the following three main stages: 1 dust removal from the exhaust gas, 2. adsorption and oxidation and regeneration, and 3 recovering sulfuric acid concentration. The detailed process is as follows:

1) Dust removal from the exhaust gas: the dust removal process is done in the dedusting tower. The relatively low cost wet dedusting or other used methods can be adopted. After dust removal, the dust content needs to be less than $0.2g/m^3$. The sulfur dioxide concentration can be more than 3000ppm. The oxygen content in the exhaust gas is preferably more than 3%. The water vapor concentration in the exhaust gas is preferably 6-12%. To those exhaust gas without need to remove dust and with relatively high oxygen and relatively low vapor content, for example the exhaust gas from the Sulfur Acid Factory, it can be recycled the sulfur dioxide after adjusting the temperature and humidity by the exhaust gas and vapor, according to the present invention.
2) Adsorption-oxidization and water-washing regeneration: after dust removal, the exhaust gas will undergo the process of adsorption and oxidization when passing through the surface of the catalyst, and the sulfur dioxide is adsorbed on the surface of the catalyst and oxidized to sulfuric acid under the action of iodine or iodide. After the desorption of sulfuric acid by water-washing, the catalyst is regenerated and recycled. The process of adsorption is done in the adsorption tower, which is filled with the fixed

tray containing the catalyst in this invention. The number of trays may be one or more storeys. The adsorption tower may be one, this tower will be alternately used by the adsorption-oxidization and water-washing regeneration, but the multiple towers are generally used and switched by turns for continuous work, that is, often one tower is regenerated by water washing, while the others are under the adsorption operation of different saturated degrees. In order to sufficiently eliminate the sulfur dioxide, the method according to this invention employs the multiple adsorption towers which are switched to work by turns, that is, when one tower is regenerated by water washing, the others are under the adsorption operation of different saturated degrees., When the exhaust gas is adsorbed and oxidized in the tower, the temperature of the exhaust gas keeps 50-70□. After adsorbing a certain amount of sulfuric acid, the catalyst in the adsorption tower must be water washed and regenerated so as to recycle the catalyst.

The process of water washing regeneration of this invention is as follows:

a) Air will be first pumped to oxidize to the iodine ion to iodine before the water washing.
b) The sulfuric acid of different concentration dilute and water will be respectively sprayed into the catalyst tower to wash it, and in the end the catalyst will be soaked in aqueous solution for a certain time to further wash the sulfuric acid away from the surface of catalyst and at the same time remove the dust that covers the surface of catalyst.
c) After water washing, the wet catalyst tower will be heated to 90-100□ by the hot vapor, and the process of regeneration will then complete.
d) Compensation of the active component: After the long time of operation, the activity of catalyst is decreased because of the loss of iodine and the active component should be compensated during the water washing regeneration. In this invention, the iodine and iodide should be compensated, if the iodine content is lower than 0.2%. After the adsorption tower in need of compensation of the active component is regenerated by water-washing, the iodine solution measured will be added into the tower from the top of the catalyst tower, and then the tower is switched to adsorption process with the exhaust gas being pumped into, the activity of this catalyst tower will then be gradually recovered to the original level.

3) Concentration of the reclaimed sulfuric acid: the sulfuric acid of concentration20-30% can be obtained, after the adsorption tower is washed by dilute sulfuric acid of different concentration dilute. The recycled sulfuric acid can be further concentrated by one of the known concentrating methods that result in ideal concentration.

Example 1: the preparation of the catalyst

The catalyst of this invention will be obtained by the following process: to fill the activated carbon in the grade bed of the catalyst, then to add the iodine

solution measured into the tower to wet all the activated carbon without surplus solution; to pump into the hot air with temperature of 100-200□ from the bottom of the catalyst tower, and stir and dry under the condition of boil, the time of heating is 1-10 h, the velocity of air is 0.1-10m/s, the quantity of air is corresponding to the volume of the catalyst 1000-20000/h.

Example 2: the method to reclaim sulfur dioxide from the exhaust gas

The process to reclaim sulfur dioxide from the exhaust gas is shown in the figure 1: 1, the tower of removal dust; 2,3,4,5 the adsorption tower; 6 the concentrating tower. A is the exhaust gas from factory; B is the exhaust gas after the sulfur dioxide is reclaimed; C is the nozzle by which water or dilute acid are sprayed during the regeneration. D is the exit zone for concentrated sulfuric acid. After the dust removal, the dust content of the exhaust gas is less than 0.2g/m^3, the oxygen content is more than 3%, the vapor content is 6-12%, the temperature of the exhaust gas is 55-75□.The process of adsorption and regeneration is done in the four towers, among which, the 2 to 4 towers are adsorbing and oxidizing the exhaust gas. When the sulfur dioxide content of the exhaust gas reaches 0.3%-0.4%, the space velocity of 400-500/h can be employed and the adsorption and oxidization is done for 18-20 hours in the three towers. The process of regeneration is under way in tower 5: at first, the air is pumped to oxidize, and then the sulfuric acid of different concentration is sprayed□ in the end the catalyst is soaked in the aqueous solution. The process of water-washing regeneration will last for four hours. After the dilute sulfuric acid discharged, the grade bed of the catalyst will be heated to 100□by the hot vapor, and the regenerating process of the adsorption tower will thus complete after heating. The four towers will be switched by turns between adsorption and water washing regeneration, therefore the entire process of reclaiming sulfur dioxide will work continuously.

Example 3: to reclaim the sulfur dioxide from the exhaust gas of PowerStation.

The flux of exhaust gas is 5000m^3/h, and said the equipments, the process and method in the example 2 will be employed, and the volume of catalyst is approximate 4.5m^3, the time of operation is 1800 hours, the regeneration in the four towers is done approximate 100 times, the active component of the catalyst need not to be compensated. The result of operation for the two times is shown in the table 1.

Table 1 Recycle of the sulfur dioxide from the exhaust gas and purification

	First time	Second time
The concentration of Sulfur dioxide (ppm)	3530	3860
The Space velocity (h^{-1})	414	502
The average conversion of Sulfur dioxide (%)	95	91
The amount of Sulfur dioxide adsorbed (g/100g catalyst)	13.3	15.4

Example 4: reclamation of the Sulfur dioxide from the exhaust gas of the sulfuric acid factory

The flux of the exhaust gas treated is 15,000m^3/h, the time of operation is 2,000 h, and said the amount of catalyst and the equipments in the example 2, 3 will be employed. The result of operation for the two times is shown in the table 2:

Table 2 Recycle of the sulfur dioxide from the exhaust gas and purification

	First time	Second time
The concentration of Sulfur dioxide (ppm)	3372	5971
The Space velocity (h^{-1})	450	450
The average conversion of Sulfur dioxide(%)	96.6	98.0
The amount of Sulfur dioxide adsorbed (g/100g catalyst)	20.2	19.5

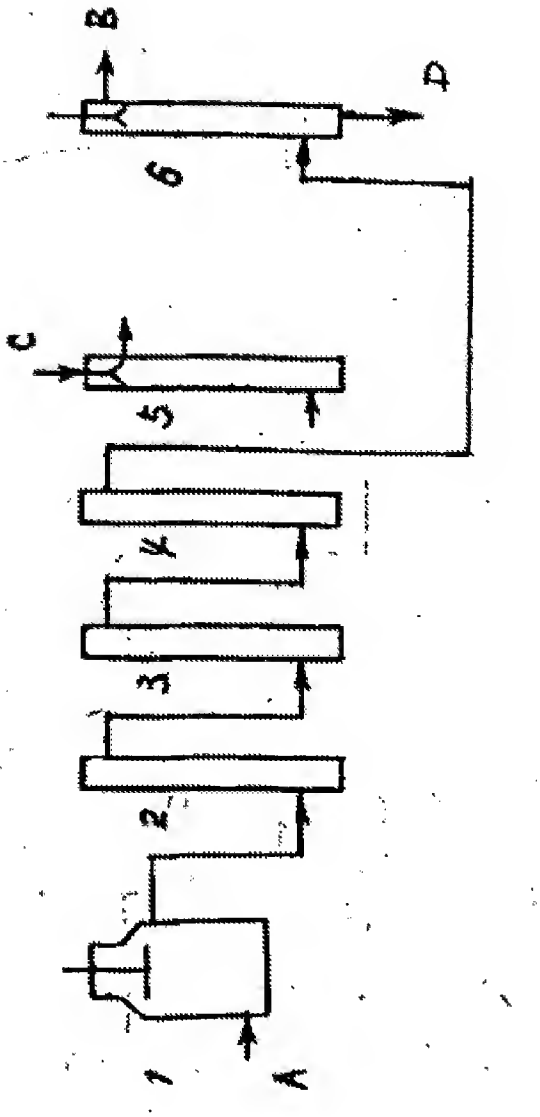

Figure 1